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Alkoxylated p-Phenylenevinylene Oligomers: Synthesis and Spectroscopic and Electrochemical Properties.

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Abstract: Twenty-one n-alkoxy substituted phenylenevinylene oligomers were synthesized, varying in size, number and position of the OR groups. IR,MS and solubility data are presented. NMR measurements provided the molecular structure as well as information about conformations and molecular dynamics. UV and of cyclic voltammetric data give correlations of chemical structure (number and position of OR substituents) with separate HOMO and LUMO energies. © 1997 Elsevier Science Ltd.

INTRODUCTION

Para-phenylenevinylene (PPV) oligomers are studied because of their potential applications as active materials in light emitting diodes, coatings on electrodes and as non-linear optical materials¹⁻³. In continuation of our research programme on functional dyes, we investigated twenty one PPV oligomers containing alkoxy substituents varying in number, size and position on the phenyl rings. The group can be divided into four subgroups: (i) seven stilbene derivatives (DP series), (ii) seven 1,4-bis[2-(4-alkoxyphenyl) ethenyl] benzenes (TP series), (iii) three 2,5-dialkoxy-1,4-bis[2-phenylethenyl] benzenes (TC series) and (iv) four 2,5-dialkoxy-1,4-bis[2-(3,4,5-trimethoxyphenyl) ethenyl] benzenes (TO series). Fig. 1 shows the structural formulas and numbering of these and some other relevant compounds. We report here on their synthesis and characterization by IR, MS, NMR (¹H and ¹³C), UV-Vis (absorption and emission) and cyclic voltammetry (CV). In addition to structural data, information is also given about solubilities in organic solvents as well as on conformational preferences and ring mobilities. The combined UV and cyclic voltammetric results allow an extended correlation between structural details and spectroscopic properties.

EXPERIMENTAL PART

Synthesis

All PPV oligomers were prepared under nitrogen protection via the Wittig reaction^{4.5} using sodium ethanolate as

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Figure 1: Structural formulas, numbering of the compounds under investigation and numbering of the atoms for NMR chemical shifts assignments.

the base and ethanol as the solvent. **Fig. 2** shows the formation of TO4 as an example. In these processes, coupling is achieved between appropriately substituted aldehydes and (mono- or bis-) phosphonium salts of suitably substituted mono- or bis-halomethylated benzenes. Benzaldehyde (TC series) and 3,4,5-trimethoxybenzaldehyde (TO series), as well as the bis(triphenylphosphonium) salt of 1,4-bis(chloromethyl) benzene (DP and TP series) are commercially available. Williamson syntheses^{6,7} were employed to prepare p-alkoxybenzaldehydes (DP and TP series) from p-hydroxybenzaldehyde, and p-alkoxy-methylbenzenes (DP series) from p-cresol, and p-dialkoxybenzenes (TC and TO series) from hydroquinone, the latter under nitrogen protection. The p-alkoxy-methylbenzenes were methylbrominated by Wohl-Ziegler bromination^{8,9}, followed by conversion of the products into the monophosphonium salts by triphenylphosphine using p-xylene as the solvent^{4,5}. The p-dialkoxybenzenes were bis-chloromethylated as described in the literature^{10,11}, and the products transformed into the bisphosphonium salts using dimethylformamide as the solvent⁵. **Table 1** summarizes yields and melting points or boiling points of the intermediate compounds. It should be noted that the Wittig synthesis of the compounds of the DP series results in compounds in the *trans-* configuration, whereas the compounds of the **TP**, TC and TO series are obtained as mixtures of the *cis, cis, cis, trans-* and *trans, trans-* configurations.



Figure 2: Formation of TO4 by a Wittig reaction.

Com- pound ^{a)}		Alkoxy	group	and	b.p.	or	m.p.	Yield
	CH ₃	C ₂ H ₅	n-C ₃ H ₇	n-C4H9	n-C ₆ H ₁₃	n-C ₈ H ₁₇	n-C ₁₆ H ₃₃	Range
РХ			67/5°	76/5°	96/5°	118/5°	42	50-80
PB		69-70	48-49	42-43				50-70
РА			112/5°	120/5°	125/5°	137/5°	48	80-90
PBB	124/5°		98/5°	110/5°	140/5°	159/5°	56	60-80
ACB	165-166	146-147	82-84	84-86				40-60
ррв	234		223	197	198	138	156	40-95
PCB	216-218	264-266	272-274	276-278		}		70-90
DP	218	206	200	192	170	142	134	50-60
TP ^{b)}	302-304	300-303	294-298	315-318	294-298	280-284	235-240	70-95
TO ^{b)}	256-257	212-215	224-226	222-224				50-80
TC ^{b)}	176	185-186	178-180	132-134				40-60

Table 1: Yields (%) and melting points (°C) or boiling points (in °C/mm Hg) of intermediate and final products.

^{a)} PX: p-alkoxymethylbenzenes; PB: p-dialkoxybenzenes; PA: p-alkoxybenzaldehydes; PBB: p-alkoxy(bromomethyl)benzenes; ACB: 2,5-dialkoxy-1,4-bis(chloromethyl)benzenes; PPB: triphenylphosphonium salts of p-alkoxybromomethylbenzenes; PCB: bis(triphenylphosphonium salts) of 2,5-dialkoxy-1,4-bis(chloromethyl) benzenes.

^{b)} after isomerisation to *trans, trans*-configuration, ^{c)} a/b signifies a boiling point of a °C at b mm Hg.

Compound		cis, cis-		cis, trans-		trans, trans-
	%	ret. time	%	ret. time	%	ret. time
TPI	28	6.55	61	7.62	11	8.38
TP2	29	6.90	48	7.97	23	8.76
TP3	29	7.48	54	8.58	18	9.37
TP4	53	8.10	35	9.22	12	10.00
TP6	38	9.22	47	10.38	15	11.15
TP8	36	10.20	50	11.35	14	12.12
TP16	40	13.66	46	14.55	14	15.30
TC2	37	8.23	43	9.19	20	10.06
тС3	46	8.56	42	9.49	12	10.25
TC4	43	9.06	28	9.93	29	10.67
TOI	10	11.87	41	12.86	49	13.94
то2	4	10.68	64	11.76	32	12.76
тоз	33	11.10	45	12.04	22	13.06
т04	39	11.57	40	12.50	21	13.54

Table 2: Isomer contents (in %) of the oligomers in the TP, TC and TO series obtained in the Wittig syntheses, together with their retention times (in min.) determined by high temperature gas chromatography¹².

The isomer contents of these mixtures, determined by high temperature gas chromatography¹², are given in **Table 2** together with the retention times of the individual isomers. Although it is possible to separate them by high performance liquid chromatography¹², we did not do so. Instead, they were converted into the *trans, trans*-configuration by refluxing the mixture with a catalytic amount of iodine in p-xylene for 4 hours. **Table 1** gives yields of the *cis/trans*- mixtures and melting points of the pure *trans, trans*- isomers.

Characterization

High temperature gas chromatograms were recorded on a Hewlett Packard HP 5890 gas chromatograph equipped with a simulist column (length: 6 m; external diameter: 0.53 mm). The temperature programme was set from 40 to 400°C with a rate of 20°C/min.

Infrared spectra were recorded on a Nicolet 5 DXB-Fourier transform infrared spectrophotometer equipped with a diffuse reflectance cell.

Electron impact (70 eV) mass spectra were measured on a VG 70 SEQ hybrid mass spectrometer using a direct inlet probe.

¹*H*- and ¹³*C*- nuclear magnetic resonance spectra were recorded on a Varian Unity spectrometer, used in conjunction with a Sun Spark (Palo Alto, CA) data system and operating at 400 MHz (for ¹H) and at 100 MHz (for ¹³C). The spectra were taken at room temperature of solutions in CDCl₃ using tetramethylsilane as the internal standard.

UV-Vis absorption spectra of 10^{-5} M solutions in CH₂Cl₂ have been measured at room temperature on an UVICON 930 spectrophotometer operating between 250 and 500 nm. Hence, the spectra most likely represent features of monomeric molecules. Fluorescence emission spectra have been measured on a Perkin Elmer spectrophotometer using 10^{-5} M solutions in CH₂Cl₂, exciting the sample with UV radiation at λ =300 nm. Fluorescence excitation spectra of CH₂Cl₂ solutions of the compounds in the DP series were recorded on the same instrument, taking three different emission wavelengths (λ (emi) = 400, 440 and 460 nm). Similarly, excitation spectra of the compounds of the other series were taken at λ (emi) = 440, 460 and 500 nm. The variation in emission wavelength led in no case to a change in the excitation spectra.

Cyclic Voltammetry Cyclic voltammograms of DP4, TP4, TC4 and TO4 were obtained at scan rates of 100, 250 and 500 mV sec⁻¹, using an EG & G PAR model 273 potentiostat/galvanostat controlled by an IBM P70 computer. A three-electrode configuration contained in an undivided cell was used. The cyclic voltammetry measurements in the oxidation region were performed using 0.1 M tetrabutylammonium borotetrafluoride (TBABF₄) in CH₂Cl₂. The reference electrode was an Ag wire electrode in 0.1 M AgNO₃ in acetonitrile, separated from the other electrodes by a diaphragm. The working electrode was a Pt tip electrode with a diameter of 2 mm and the counter electrode was a Pt mesh electrode. The measurements in the reduction region were performed using a solution of 0.1 M TBABF₄ in N-methylpyrrolidone. The reference electrode was an Ag wire electrode a Pt mesh electrode.Cyclic voltammetry measurements on the above and 15 other (mostly less soluble) compounds were performed in the oxidation region using an EG & G PAR model 175 potentiostat coupled with an EG & G PAR model 174A polarographic analyser. The scan rate was 100 mV sec⁻¹. As electrolyte a solution of 0.1 M LiClO₄ in acetonitrile was used and a saturated calomel electrode (SCE) was taken as the reference electrode. All measured potentials are quoted against ferrocene as the standard.

RESULTS AND DISCUSSION

Wittig Synthesis and Characterization

The benzylides employed in this work are generally classified as semi-stabilized ylides¹³, because they have significant electron delocalization in the carbanion, but can not be isolated. The normal reaction of semi-stabilized triphenylphosphonium benzylides with aldehydes produces mixtures of Z- and E- alkenes nonstereospecifically^{13,14}. Indeed, we find in the TP, TC and TO series the *cis, trans*- forms as the most abundant isomers, and insignificantly larger abundances of the *cis, cis*- isomers compared to the *trans, trans*- isomers (**Table 2**). In the DP series, however, we observed only the *trans*- isomers. These two sets of observations, however contrasting are not contradictory, because no precautions were taken to prevent isomerization in the later stages of the synthetic process.

The IR spectra of the Wittig mixtures of all oligomers are much alike in overall appearance. For example, they show absorption bands due to alkyl C-H stretchings at 2960 and 2870 cm⁻¹, to phenyl ring breathings at 1610 and 1510 cm⁻¹, and to C-O stretchings at 1275 and 1030 cm⁻¹. The latter bands are usually the most intense in the spectra. Small, but highly characteristic differences reveal the structural backbone. For example, a signal at 565 cm⁻¹ is characteristic of a *cis*- configuration, while signals at 640 cm⁻¹ and 965 cm⁻¹ (out-of-plane H-C=C-H bending) are characteristic of a *trans*- configuration¹². The substitution pattern of the phenyl rings shows¹⁵ in the presence of absorption bands at about 900 and 720 cm⁻¹ (5 adjacent H atoms; TC series), near 830 cm⁻¹ (2 adjacent H atoms; DP and TP series), and near 880 cm⁻¹ (1 adjacent H atom; TO series).

In the electron impact mass spectra of the oligomers (see **Table 3**) the M^+ ion is always the most abundant ion, and the m/z- values are in agreement with of the empirical formulas. The M²⁺ ions often of importance in this type of compounds, are insignificant in the DP and TP series, but show a relative abundance of about 5% in the TC series and of about 15% in the TO series. This points to the increased tendency of the molecules to lose an electron of the alkoxy-substituted central ring. Regarding structural information, the oligomers being (higher) dialkyl aromatic ethers are expected¹⁶ to show the loss of one or two R radicals from M^+ , and expulsion of one or two C_nH_{2n} molecules via a Mc Lafferty rearrangement, resulting in the highly characteristic odd electron ions at $(M-C_nH_{2n})^+$ and $(M-2C_nH_{2n})^+$. Furthermore, elimination of R yields an even electron ion $(M-R)^+$ which may eliminate C_nH_{2n} leading to $(M-R-C_nH_{2n})^+$. The latter ion may also arise by elimination of R from $(M-C_nH_{2n})^+$. These processes are indeed observed, but some details may be noted. First, the methoxy derivatives can not expel C_nH_{2n} and show as characteristic¹⁶ ions (M-CH₃)⁺, (M-CH₂O)⁺ and (M-OCH₃)⁺. Second, in the DP and TP series the loss of R is the most important process for $R \le C_2 H_5$, whereas the loss of $2C_n H_{2n}$ becomes the major pathway for larger R. In the TC series the ions at $(M-R)^+$, $(M-C_nH_{2n})^+$ and $(M-2C_nH_{2n})^+$ are almost equally abundant. The loss of 2R occurs only in the TC series to a small, but significant extent. The TO series shows a deviating fragmentation behaviour. The major process is the gradual fragmentation of the alkyl radical, with results in the typical $(M-C_nH_{2n+1})^+$ peaks. Third, some compounds of the DP series show significant peaks at m/z = 165, m/z = 153 and m/z = 152, possibly corresponding to fluorenyl, biphenyl and biphenylenyl type ions¹⁷.

Nuclear Magnetic Resonance and Conformational Aspects.

The ¹H and ¹³C chemical shifts are summarized in **Table 4** and **5**, respectively. With the exception of TP, for which also a *cis, cis*- spectrum could be unraveled from a *cis/trans*- mixture, only the data for the *trans, trans*- compounds are given. The low solubility of the TP series precluded the recording of the ¹³C-NMR spectra.

Compound	M*.	M ²⁺	$[M-C_nH_{2n}]^+$	[M-R] ⁺	$[M-2C_nH_{2n}]^+$	$[M-R-C_nH_{2n}]^+$	[M-2R] ⁺
DP1	240(100)	120(8)		225(60)			210(4)
DP2	268(100)		240(20)	239(60)	212(20)	211(55)	
DP3	296(100)		254(28)	253(22)	212(55)	211(40)	
DP4	324(100)		268(10)		212(70)	211(30)]
DP6	380(100)		296(21)		212(56)	211(27)	
DP8	436(100)	į	324(15)		212(60)	211(30)	
DP16	660(100)		436(8)		212(40)	211(22)	
TPI	342(100)	171(16)		327(8)			
TP2	370(100)			341(8)			
TP3	398(100)		356(18)	355(18)	314(25)	313(8)	Ì
TP4	426(100)		370(10)	369(10)	314(20)	313(5)	
TP6	482(100)		398(18)	397(10)	314(28)	313(5)	
ТР8	538(100)		426(10)	425(8)	314(20)		
TC2	370(100)	185(8)	342(10)	341(20)	314(5)	313(10)	312(15)
тС3	398(100)	199(8)	356(18)	355(20)	314(25)	313(18)	312(10)
TC4	426(100)	213(5)	370(22)	369(19)	314(22)	313(10)	312(5)
Compound	M ^{+.}	M ²⁺	[M-CH ₃] ⁺	$[M-C_2H_5]^+$	$[M-C_3H_7]^+$	[M-C₄H ₉] ⁺	
TO 1	522(100)	261(18)	507(38)				
то2	550(100)	275(15)	535(15)	521(5)			
тоз	578(100)	289(15)	563(10)	549(10)	535(5)		
т04	606(100)	303(13)	591(8)	577(5)		549(5)	

Table 3: Electron-impact (70 eV) mass spectral data; m/z-values with relative intensities (% of base peak) in parentheses.

The shifts are assigned with the help of standard chemical shift increments¹⁸ and confirmed from 2Dheteronuclear correlation (Hetcor) spectra. The positions, intensities and coupling patterns of the NMR signals provide unequivocal proof of the structures. For example for TC4, one notes four types of aromatic protons that can be assigned with certainty. The signal at $\delta = 7.12$ ppm, being a singlet, belongs to H(3B) = H(6B). At $\delta =$ 7.52 ppm a double doublet appears, which is assigned to H(2A), with ³J(2A,3A) = 8.1 Hz and ⁴J(2A,4A) = 1.5 Hz, and at $\delta = 7.24$ ppm, the triple triplet is assigned to H(4A) with ³J(3A,4A) = 6.8 Hz and ⁴J(2A,4A) = 1.5 Hz. Hence, the quasi- triplet at $\delta = 7.35$ ppm must be ascribed to H(3A) and indeed reveals the coupling constants ³J(2A,3A) = 8.1 Hz and ³J(3A,4A) = 6.8 Hz. Furthermore, at $\delta = 7.48$ ppm and $\delta = 7.13$ ppm double doublets are observed. They are assigned to H(1O) and H(2O), respectively, analoguous to the assignment in TO series¹². The value ³J(1O,2O) = 16.5 Hz proves the *trans, trans*-configuration. Finally, at $\delta = 4.05$ ppm, $\delta = 1.85$ ppm, $\delta = 1.58$ ppm and $\delta = 1.05$ ppm the signals of H(1S), H(2S), H(3S) and H(4S), respectively, are seen with ³J(1S,2S) = 6.4 Hz and values of about 7 Hz for the other vicinal H,H-coupling constants in the alkoxy chain. The Hetcor spectrum and the not-decoupled ¹³C-spectra prove the correctness of the ¹³C shift assignments. The assignments of TC4 were then transferred to the other compounds in the TC series. Assignments of shifts in the DP, TP and

		Ring A		Ring B		Olefinic	link	Alkoxy	Chain			0CH3	uo	
	H(2A) H(6A)	H(3A) H(5A)	H(4A)	H(3B) H(6B)	H(2B) H(5B)	H(10)	H(20)	H(1S)	H(2S)	H(3S) H((n-1)S)	H(nS)	3A	4A	
DP1	7.42	6.88				6.93		3.82						
DP2	7.40	6.87				16.9		4.04			1.42			
DP3	7.40	6.87				6.91		3.93	1.81		1.04			
DP4	7.40	6.87				6.91		3.97	1.77	1.50	0.98			
DP6	7.40	6.87				6.91		3.97	1.77	1.31-1.50	16.0			
DP8	7.40	6.87				6.91		3.96	1.78	1.25-1.50	0.89			
DP16	7.40	6.87				6.91		3.96	1.78	1.15-1.50	0.89			
TP1	7.44	6.89		7.47	7.47	7.04	6.93	3.83						³ J(2A,3A)= 8.6 Hz;
TP2	7.44	6.89		7.46	7.46	7.06	6.96	4.06			1.42			³ J(10,20)= 16.2 Hz
TP3	7.44	6.89		7.46	7.46	7.06	6.96	3.95	1.82		1.25			3 J(1S,2S) = 6.4 Hz
TP4	7.44	6.89		7.46	7.46	7.06	6.95	3.98	1.82	1.55	10.1			³ J(n-1S,nS)= 7.4 Hz
941	7.46	6.89		7.46	7.46	7.04	6.97	3.98	1.82	1.35-1.55	16.0			
TP8	7.44	6.88	_	7.46	7.46	7.06	6.96	3.98	1.82	1.30-1.55	0.89			
TP16	7.43	6.88		7.46	7.46	7.14	6.94	3.95	1.82	1.30-1.55	0.89			
TC2	7.50	7.32	7.21	7.10		7.45	7.09	4.09			1.45			$^{3}J(3A,4A) = 6.8 \text{ Hz};$
TC3	7.53	7.35	7.24	7.12		7.48	7.13	4.02	1.89		1.12			³ J(2A,3A) = 8.1 Hz;
TC4	7.52	7.35	7.24	7.12		7.48	7.13	4.05	1.85	1.58	1.05			³ J(2A,4A) = 1.5 Hz
101	6.77			7.12		7.36	7.06	3.94				3.92	3.88	
T02	6.77			7.12		7.36	7.06	4.14			1.49	3.92	3.88	
T03	6.76			7.12		7.38	7.06	4.03	1.90		1.13	3.92	3.88	
104	6.76			7.12		7.38	7.06	4.07	1.86	1.60	1.03	3.92	3.88	
TPI cis	7.35	6.77	7.46			6.53	6.48	3.79						³ J(2A,3A) = 8.4 Hz ³ J(10,20 = 12.2 Hz

Table 4: ¹H NMR chemical shifts (in ppm, relative to TMS) of the oligomers in CDCl₃ solution. Of TP1 the cis, cis- and trans, trans-isomer are given, of the other oligomers only **trans. trans.** isomers are given: See Fig. 1 for numbering of the atoms: H(iA) is attached to C(iA).

		•															ſ
		King A				King B		okef.	Ĕ	Alkoxy	chain	0C _n H _{2h1}				OCH ₃	5
	C(1A)	C(2A) C(6A)	C(3A) C(5A)	C(4A)	C(1B) C(4B)	C(2B) C(5B)	C(3B) C(6B)	C(10)	C(20)	C(1S)	C(2S)	C(3S) C((n-3)S)	C((n-2)S)	C((n-1)S)	C(nS)	3A	4A
DPI	130.6	127.4	114.2	159.1				126.3		55.3							
DP2	130.5	127.4	114.8	158.4				126.2		63.5					14.8		
DP3	130.4	127.4	114.8	158.7				126.2		69.7				22.6	10.5		
DP4	130.4	127.4	114.8	158.7				126.2		67.8			31.4	19.3	13.8		
DP6	130.4	127.4	114.8	158.7				126.2		68.2	29.3	25.7	31.6	22.6	14.0		
DP8	130.4	127.4	114.8	158.7				126.2		68.2	29.4	26.1-29.5	31.8	22.7	14.1		
DP16	130.1	127.4	114.8	158.4				126.2		68.2	29.7	26.1-29.4	32.0	22.7	14.1		
TCI	137.9	126.6	128.6	127.4	127.4	151.6	109.3	123.3	129.0	56.4							
ជ្ជ	138.1	126.6	128.7	127.4	127.4	151.1	111.1	123.4	128.9	65.3					15.1		
Ð	138.1	126.6	128.6	127.4	127.1	151.2	0.111	123.6	128.9	71.2				22.9	10.8		
17	138.1	126.5	128.6	127.4	127.3	151.2	110.9	123.7	128.9	69.3			31.6	19.5	13.9		
ē	133.6	104.0	153.4	138.2	126.5	151.6	109.4	122.7	129.1	56.4						56.2	6.09
102	133.7	104.0	153.4	138.2	126.9	151.0	111.1	123.1	128.9	65.2					15.0	56.2	6.09
103	133.8	104.0	153.5	138.2	127.1	151.2	111.1	123.1	128.8	71.4				23.0	10.8	56.2	60.9
104 1	133.8	103.9	153.5	138.2	127.0	151.2	110.9	123.1	128.8	69.5			31.9	19.6	14.0	56.2	6.09

Table 5: ¹³C NMR chemical shifts (in ppm, relative to TMS) of **trans, trans**-oligomers in CDCl₃ solution.

^{a)} Data taken from ref 19, and reinterpreted.

TO series proceeded as outlined above and were helped by previous assignments of TO1¹² and *trans*-stilbene²⁰. One notes that great similarities exist between the TC and TO series as well as a great resemblance between the DP and TP series. As stated above, the shift values of cis, cis-TP1 were assigned from the ¹H-NMR spectrum of the cis/trans- mixture, proving the configuration from ${}^{3}J(H(10),H(20)) = 12.2$ Hz, as well as showing the similarity with the spectrum of cis, cis- TO1, reported before¹². Upon further inspection, Tables 4 and 5 also supply information about the conformational aspects of the compounds. Firstly, in the TC and TO series the chemical shift of C(3B) is significantly below its reference value (114.5 ppm) and the shift of H(3B) is significantly above the reference value (6.83 ppm, ref. 18). The interpretation^{21,22} is that the atoms C(3B) and H(3B) are in the ortho-syn-position to the nearest olefinic link (see Fig. 3). When the latter atoms are in orthosyn-position, the atoms C(5B), C(2B) must be in ortho-anti-position to the nearest olefinic link and consequently the shift $\delta(C(2B))$ should be, and indeed is observed, significantly above the reference value (150.4 ppm). The proposed conformation of the alkoxy groups in ring B with respect to their adjacent olefinic links (ortho-alkoxyanti) is observed in an X-ray analysis of crystalline trans, trans-2,5-dimethoxy-1,4-bis[2-(2,4-dimethoxyphenyl) ethenvl] benzene²³, and is attributed to an interaction of type H(1O)-O(2B). If the interaction also accounts for the conformation in solution, one may expect shifts of olefinic protons participating in such interactions to differ from those that do not participate. The distinction may even extend to the attached olefinic carbon atom. These differences are indeed found. Taking as reference chemical $shifts^{12}$: H(1O) = H(2O) = 7.00 ppm, C(1O) = 125.0ppm and C(2O) = 129.8 ppm, one notes in the TC and TO series a significant downfield shift for H(1O) and an upfield shift for C(1O). In all series atoms H(2O) and C(2O) and most importantly atoms H(1O) and C(1O) in the TP series are not engaged in H---O interactions and their shift values are close to the reference shifts. Next, we observe in all series the equivalence of C(2A) and C(6A), as well as of H(2A) and H(6A). Additionally, in the TP series all H(B) atoms are equivalent. These equivalences are not imposed by symmetry, but indicate in all series rotational freedom around the bond C(1A)-C(2O) as well as around the bond C(4B)-C(1O) in the TP series. Conformational freedom is probably attended by the absence of ring substituents ortho to the olefinic link. In accordance with this idea are the lower barriers to the ring rotation calculated for the free state of trans, trans-1,4bis[2-(3,4,5-trimethoxyphenyl) ethenyl] benzene²³, in which neither ring A nor ring B carries an orthosubstituent, compared to the higher ring rotation barriers calculated for the free state of trans, trans-2,5dimethoxy-1,4-bis[2-(2,4-dimethoxyphenyl) ethenyl] benzene²⁴, in which both rings A and B carry ortho substituents. Further evidence for the configurational and conformational assignment was sought and found from C,H coupling constants. For example, in trans, trans-isomers the positioning of the atoms C(1A) and H(1O) as well as of C(4B) and H(2O) is Z. We observed (Table 6) in TC4 the values ${}^{3}J(C,H) = 6.1$ Hz and 5.0 Hz. respectively, in close agreement with the corresponding coupling constants in *trans, trans*-TO1¹².



Figure 3: Proposed conformation of trans, trans-TC (and TO) compounds in solution. We label the position of C(2,B) (carrying an OCH₃ group) as ortho-anti with respect to the nearest olefinic link and hence, the position of C(3,B) (carrying a H atom) as ortho-syn.

Furthermore, we recently estimated¹² a ³J(C,H) value for a *syn*-position at 3.9-4.5 Hz, for a rotating position at 4.5-5.2 Hz, and for an *anti*-position at 5.2-5.7 Hz. Such values are found (**Table 6**) for ³J(C(2B), H(1O)), ³J(C(2A), H(2O)) and ³J(C(3B), H(1O)), respectively, thus supporting the conclusions drawn from the chemical shift data.One may also note that as before¹², the vicinal coupling constant between an olefinic carbon and a H atom on a rotating phenyl ring is slightly larger than its counterpart on a non-rotating ring (cfr ³J(C(2O), H(3A)) and ³J(C(1O), H(3B))).

To end this section, we note that the values ${}^{3}J(H, H) \approx 7$ Hz and ${}^{3}J(C, H) \approx 4$ Hz observed in the OR groups point to an extended conformation of the alkoxy chains with most torsion angles H-C-C-H and H-C-C-C of about 60°.

C atom	H atom	Туре	Value	C atom	H atom	Туре	Value
1A	3A/5A	31	7.7	3B	3B	'J	156
1A	10	³ J	6.1	3B	10	3J	5.4
2A/6A	2A/6A	ı	158	10	10	1 ¹	154
2A	6A/4A	³ J	7.2	10	3B	³ J	4.2
2A/6A	20	³ J	5.0	20	20	l,1	151
3A	3A	¹ J	161	20	2A/6A	³ J	4.6
3A	5A	³J	7.6	15	15	,1	143
4A	4A	³ Ј	161	15	35	³ J	4.2
4A	2A/6A	³ J	7.6	25	25	¹ J	125
1B	3B	³ J	~9.0	25	4S	³ J	-4
1B	20	³J	~5.0	3S	3S	1 ¹	125
2B	6B	¹ J	7.0	3S	15	³ Ј	4.1
2B	10	³ J	4.0	4S	4S	J	125
3B	3B	¹ J	156 .	4S	2S	³ J	4.1

Table 6: Selected C, H coupling constants (in Hz) of trans, trans- TC4 measured in CDCl₃ solution.

Table 7: Room temperature solubilities (g/100 ml solvent) of oligomers⁴.

	Chloro- form	Dichloro- methane	THF	Aceto- nitrile		Chloro- form	Dichloro- methane	THF	Aceto- nitrile
DP1	0.29	0.30	0.25	0.018	TC1	17.60			
DP2	0.70	0.49	0.74	0.021	TC2	37.60	40.43	42.80	0.54
DP3	0.83	0.56	0.86	0.023	TC3	42.28	40.82	38.58	0.56
DP4	1.00	0.67	1.04	0.024	TC4	56.20	41.76	33.23	0.60
TPI	0.006	0.005	0.012	< 0.001	TO2	30.10	7.13	0.32	0.07
TP2	0.020	0.008	0.030	< 0.001	тоз	33.86	10.64	0.84	0.06
TP3	0.024	0.008	0.035	< 0.001	т04	40.96	14.48	1.06	0.03
TP4	0.043	0.010	0.050	< 0.001					< 0.001

a) DP series trans-isomers; TP, TC, and TO series cis/trans- mixtures.

Solubilities.

Room temperature solubilities (g/100 ml solvent) were determined by adding aliquots of 0.1 ml solvent to a known quantity of the powdered oligomers until total dissolution. As solvents, chloroform, dichloromethane, tetrahydrofuran and acetonitrile were tested. **Table 7** gives the results for the *trans*- isomers of the DP series. For the other series, the solubilities of the *trans*, *trans*- isomers were too low to be measured, the solubilities of the *cis/trans*- mixtures (see **Table 2** for isomer composition) are given instead. One may note that chloroform and dichloromethane are the best solvents for the oligomers. Except for the TO series tetrahydrofuran is also a good solvent. The size of the alkoxy substituents has only a minor influence on the solubility although the butoxy-substituted compounds invariably have the highest solubility. The position of the substituents on the phenyl rings, however, has a significant influence. Solubility is much higher for compounds with substituents on the central phenyl ring than of those substituted on the peripheral phenyl rings: e.g. the solubility of TP2 is about 2000 times lower than that of TC2 in the same solvent. The introduction of extra methoxy groups on the peripheral rings (TO series) even lowers the solubility to a some extent.

UV spectroscopy.

Results of the UV experiments on all-*trans*-isomers are summarized in **Table 8**. Fig. 4 and Fig. 5 show examples of absorption, emission and excitation spectra typical for the series of compounds under investigation. For easier comparison we give normalized intensities in the ordinate of Fig. 4, i.e. one peak of each spectrum is used to scale the spectra onto each other. Two conclusions could immediately be made, applying equally to the three types of spectra. First, the size of the alkoxy groups has practically no influence. Second, from the shape of the spectra, two subgroups can be distinguished, namely TC and TO compounds on the one hand, and TP and DP compounds on the other. Because of this the analysis of absorption, emission and excitation spectra is considerably simplified.

Absorption Spectra. We start discussing the absorption spectra and note a strong resemblance between the DP spectra and those of trans-stilbene, trans-3-methoxystilbene and trans-4-methoxystilbene reported by Huysmans²⁴. Trans-stilbene shows an absorption envelope at 300 nm with a FWHM (full width half maximum) of about 2100 cm⁻¹. The envelope contains two peaks and one shoulder at $\lambda = 295$ nm ($\varepsilon = 2.9 \times 10^4$); $\lambda = 305$ nm $(\varepsilon = 2.74 \times 10^4)$, and $\lambda = 315$ nm ($\varepsilon = 1.8 \times 10^4$), respectively, which was attributed to a coupling of a phenyl vibration (ca. 1100 cm⁻¹) to the π , π^{*} electronic transition. Introduction of OR groups has a negligible influence on the extinction coefficients, but increases the FWHM somewhat. More importantly, from the positions of the maxima in the substituted compounds²⁴ it follows that one meta-OR causes a bathochromic shift of 1-2 nm and one para-OR a bathochromic shift of 12 nm, while two para-OR cause a red shift of 20 nm. The quasi-additivity with the number of substituents, the dependence upon position and the resemblance with the unsubstituted parent compound all point to a moderately weak mesomeric effect of the OR groups on the lowest energy π , π^{-1} . transition of stilbene. The simplest rationalisation^{25,26} is a mesomeric mixing of the n- orbital of an OR group in the π -orbitals of the stilbene chromophore. In meta-position the mesomeric mixing is absent, and the effect of the OR group is minimal. In para-position the OR group orbitals mix with the HOMO and the LUMO of the π system, which increases the HOMO energy more than the LUMO energy, causing a red shift. The additivity of increment shifts stems from a negligible interference between weakly interacting mesomeric substituents. For TP compounds a similar behaviour can be expected. Indeed two OR groups cause a bathochromic shift of 19 nm with respect to *trans*, *trans*-1,4-bis-distyrylbenzene (DSB; $\lambda_{max} = 350 \text{ nm}^{27}$), very similar to the shift in DP. Furthermore, *trans*, *trans*-1,4-bis[2-(3,4,5-trimethoxyphenyl) ethenyl] benzene (HMT; $\lambda_{max} = 372 \text{ nm}^{28}$), containing four meta and two para-OCH₃ groups, has an absorption spectrum strongly resembling that of TP4, red shifted by only 4 nm.

Turning to the TC absorption spectra there is no resemblance with either DSB nor TP4 (Fig. 5). One notes in TC4 two electronic transitions compared to one in TP4 (disregarding vibronic structure). Such behaviour points to a strong mesomeric interaction of the OR groups with the DSB chromophore. It seems that 2,5substitution in the central ring moves the S₁ and/or S₂ state close enough to the S₀ and S₁ state to make a new transition visible alongside the usual π , π^2 - transition. We prefer this over an interpretation using two rotametric forms, because the NMR spectra (see above) had indicated the presence of only one TC4 conformer in solution. Judged by the shape of the absorption and the intensity of the emission spectra, TC4 can be classified according to Nurmukhametov and coworkers ^{29,30} as a type 5 luminophor, i.e. one in which the energy of the electronic states increases in the order $S_0 < T_{\pi\pi^*} < S_{\pi\pi^*} < T_{n_{\pi^*}} < S_{n_{\pi^*}}$. Then the lowest energy transition at λ =394 nm resembles mostly the π - π^* transition of DSB and TP. It is red shifted by 17 nm relative to TP, despite the fact that both compounds carry two OR groups. Such a "2,5-disubstituent effect" was also noted in azobenzenes³¹ and is part of the rule of the distribution of auxochromes³². The same situation applies to the TO series and TO4 is expected to be red shifted by about 17 nm compared to HMT; experimentally a red shift of 21 nm is observed. To investigate the effects of strong interactions the Zeroth Order Orbital Approximation no longer suffices. In the more sophisticated Pariser-Part-Pople method³³ electron correlation and configuration interaction are taken into account in an empirical way. The method indicates inter alia the importance of additional inductive substituent effects, particularly in the strong mesomeric case. An inductive donor substituent will militate against electron transfer to the ring upon excitation, whereas an inductive acceptor will facilitate electron extraction. Some support for this may be found in the results of Wu et al³⁴ who calculated that in HMT the electron density in the central ring is higher in the LUMO than in the HOMO. Further work is in progress to investigate the nature of the effects contributing to the spectral features.

Emission spectra. Although contributions of more than one fluorescent species can not be excluded, we take it that in the emission spectra only the lowest energy π,π^* transition is fluorescent. **Table 8** shows that the $\lambda_{max}(emission)$ increase with the conjugation lengths (DP < TP < TeP) and that within the trimeric series the sequence is as in absorption (TP < TC < TO). Furthermore, the familiar crossing between absorption and emission is far from either maximum, i.e. large *Stokes shifts* occur. They indicate large (vibrational, electronic, geometric) differences between the excited state reached immediately after absorption (S₁^{abs}) and the excited state from which the emission starts (S₁^{em}), and suggest a four level energy system. It also leads to little self-absorption of emitted light. Hence, TC and TO compounds are expected -and were indeed found^{1,28}- to perform well in organic light emitting diodes and as laser dyes. By appearance, the emission spectra of DP, TP and TeP belong to one group, those of TC and TO to another, showing again the importance of 2,5- substitution on the central ring. Yet, the emission spectrum of HMT differs from any of the previous ones, indicating that not only the position, but also the number of the OCH₃ substituents influence the spectra.

Excitation spectra. We recall that the excitation spectra can be divided into a group containing the DP, TP and TeP series on the one hand and a group containing the TC and TO series on the other. **Fig. 4** gives typical examples how the excitation spectra of these two groups differ from the corresponding absorption spectra: in the TP series a small, but in the TC series a large blue shift is noted. To rationalize the behaviour one must recognize that an excitation spectrum measures the efficiencies of absorbed photons at various wavelengths to induce

fluorescence at a chosen wavelength (here 21 700 cm⁻¹). Hence, a blue shift tells that a non-radiative energydemanding process is operating on the excited state of particularly the TC and TO compounds. At this point there is little known about the nature of this process, except that its efficiency is wavelength dependent. Finally, we recall that TC and TO compounds show a non-fluorescent absorption maximum at 340 nm. This maximum occurs at the same position in the excitation spectra, but without loss of intensity. This shows that the corresponding excited state is capable of transferring its energy efficiently to the fluorescing π,π^* state.

Cyclic voltammetry

Optical band gaps ($E_{gap}(opt)$) were calculated for selected oligomers from the onset of the longest absorption wavelength at 10% of the UV peak maximum, and reduction potentials were estimated as $E_{red}^{SCE} = -E_{gap}(opt) + E_{ox}^{SCE}$. Oxidation potentials versus the standard calomel electrode (E_{ox}^{SCE}) were routinely obtained by cyclic voltammetry as peak potentials using acetonitrile solutions, and LiClO₄ as the supporting electrolyte and a scan rate of 100 mV sec⁻¹. Under these conditions the voltammograms are irreversible, indicating that the first formed radical cation has a short lifetime. The alkoxy groups on the phenyl rings, despite their mesomeric donor properties, do not sufficiently stabilize the radical cations in acetonitrile in the presence of LiClO₄.

Table 8: Wavelengths (nm) of maximum absorption, emission and excitation of the π , π^* transition of the alltrans oligomers recorded in CH₂Cl₂ solution at room temperature. Extinction values ($\varepsilon x 10^4$ in cm² M^1) are in parentheses. For TC and TO series, values of the second absorption transition are also reported.

Compound	Absorption		Emission	Excitation
	π, π*	2 nd peak	π, π*	π, π*
	$\lambda_{\max}(\varepsilon)$	$\Lambda_{\max}(\epsilon)$	λ_{\max}	λ _{max}
DP1	328(3.33)		379	
DP2	329(3.03)		380	330
DP3	330(3.46)		381	
DP4	330(3.42)		381	331
TP1	367(2.37)			
TP2	368(2.28)		433	359
TP3	369(2.61)			
TP4	369(2.57)		433	359
TeP4	379(3.56)		464	365
TC2	386(3.61)	326(3.23)	460	365
TC3	392(3.57)	325(3.20)		
TC4	394(3.46)	325(3.17)	461	366
то2	398(3.21)	341(2.68)	472	366
тоз	398(3.35)	341(2.73)		
ТО4	400(3.42)	342(2.78)	472	367



Figure 4: Typical absorption, emission and excitation intensities (arbitrary units) versus wave numbers (cm^{-1}) of TP4 (top) and TC4 (bottom).

Figure 5: Absorption spectra with extinction (ε in $cm^2 M^{-1}$) versus wavenumbers (cm^{-1}) of (top) DSB, HMT TC4 and TP4, and (bottom)TC4, TO4 (see fig 1 for compound numbering).

Results of a detailed investigation including conditions for reversible voltammograms will be reported later. Some preliminary data, however, will be given here, to support the routine values. In these experiments the compound with highest solubility of each series (i.e. DP4, TP4, TC4 and TO4) in the best solvent, dichloromethane, was taken with tetrabutylammonium borotetrafluoride as supporting electrolyte. Under these conditions, the voltammogram of DP4 at a scan rate of 100 mV sec⁻¹ showed an anodic peak at 0.69 V vs Ag/Ag⁺ (i.e. 1.03 V vs SCE), and no cathodic peak. However, at 500 mV sec⁻¹ the anodic peak is shown at 0.71 V vs Ag/Ag⁺ with a corresponding cathodic peak at 0.63 V. Furthermore, the voltammogram of TP4 exhibits (see Fig. 6), even at the scan rate of 100 mV sec⁻¹, two consecutive oxidation peak potentials at 0.69 V and 0.87 V vs Ag/Ag⁺ with their cathodic peaks at 0.62 V and 0.79 V, respectively. This indicates two oxidation steps with well separated first and second oxidation potentials, which correspond to the successive formation of a radical cation and a dication. Because of its longer conjugated system, TP4 is better able to stabilize the formed ions than DP4 and the voltammogram shows reversibility at relatively low scan rate. Interestingly, the introduction of alkoxy groups in the central ring allows the formation of single, double and triple charged cations. In TC4 they appear at 0.73 V, 0.85 V and 1.11 V, respectively, and in TO4 at 0.60 V, 0.69 V and 1.40 V, respectively (always vs Ag/Ag⁺).

Whereas we were unable to produce interpretable reduction voltammograms of acetonitrile solutions, the N-methylpyrrolidone-solvent/tetrabutylammonium borotetrafluoride-electrolyte combination together with a small sized dropping Hg electrode proved successful in producing reversible voltammograms in the reduction regime. The electrochemical reduction of DP4 and TP4 showed a reduction peak potential at 2.94 V and -2.50 V $vs Ag/Ag^+$, respectively. As in the oxidation regime the introduction of alkoxy groups in the central ring resulted in the formation of higher charged ions. TC4 as well as TO4 showed two reduction peaks, but in contrast to the

oxidation regime in both cases at about the same potentials. The results of all cyclic voltammetric measurements are summarized in Table 9. A comparison of the acetonitrile data with those of the dichloromethane data reveals that the oxidation potentials (brought to the SCE reference) agree with a root-mean-squares deviation of 0.10 V. The agreement is good despite the neglect of solvent effects. We now proceed to discuss the first oxidation and reduction potentials, leaving a discussion of the higher charged ions to a later date. We can conclude the following. First, the size of the OR group has no influence on the oxidation, nor on the reduction potentials. Second, the optical band gaps estimated from λ_{onset} taken at 10% of the peak intensity shows a root-mean-square deviation of 0.12 eV with the electrochemically determined band gaps. It means that the correlations between the

Compound	λ _{onset} (nm)	E _g opt.(eV)	E _{ox1} (V) on Pt vs SCE	E _{red} calc.(V)	E _{ox} (V) on Pt vs Ag/Ag ^{+ b)}	E _{red} (V) on Hg drop vs Ag/Ag ^{+ b)}	Egelectr.(eV)
SB ^{a)}	327	3.79	1.45	-2.38			
DP1	350	3.54	1.01	-2.53			
DP2	354	3.50	1.00	-2.50			
DP3	352	3.52	1.01	-2.51			
DP4	354	3.50	1.01	-2.51	0.69	-2.94	3.63
DP6	352	3.52	1.01	-2.51			
DP8	352	3.52	1.02	-2.50			
DSB ^{a)}	383	3.24	1.22	-2.02			
TP1	392	3.16	0.97	-2.19			
TP2	401	3.09	0.95	-2.15			
TP2 c/t mix.	393	3.15	1.15	-2.00			
ТР3	403	3.08	0.94	-2.14			
TP4	402	3.08	0.94	-2.14	0.69; 0.87	-2.50	3.19
TP4 c/t mix.	401	3.09	1.15	-1.94		<u>-</u>	
TC2	431	2.88	0.93	-1.95			
TC3	432	2.88	0.94	-1.94			
TC4	431	2.88	0.95	-1.93	0.73; 0.85; 1.11	-2.38; -2.81	3.11
HMT ^{a)}	401	3.09	0.94	-2.16			
TO1	441	2.81	0.85	-1.96			
ТО2	439	2.82	0.84	-1.98			
тоз	439	2.82	0.84	-1.98			
Т04	439	2.82	0.84	-1.98	0.60; 0.69; 1.40	-2.37; -2.77	2.97
TeP1 ^{a)}	435	2.86	0.97	-1.89			
TeP4 ^{a)}	436	2.84	0.96	-1.88			

Table 9: Oxidation and reduction potentials of selected oligomers. Values of trans, trans-isomers are given, unless specified otherwise.

^{a)} See Fig 1 for structural formulas. Data are taken from ref 37. ^{b)} The following relations were used³⁸ : $E_{ox}(SCE) = E_{ox}(Ag/Ag^+) + 0.34$ and $E_{red}(SCE) = E_{red}(Ag/Ag^+) + 0.34$.

UV absorption maxima and chemical structure also apply to the electrochemical band gaps. Third, we neglect solvent effects and take the E_{ox} -values to represent the HOMO energies and the E_{red} -values to represent the LUMO energies^{36,37}. Then, **Fig. 7** presents in a semi-quantitative way the HOMO and LUMO orbital energies of the compounds studied. Inspection of **Fig. 7** and **Table 9** shows by comparing DSB (*trans, trans*-distyrylbenzene) and TP that para-OR-substitution of the peripheral rings raises the HOMO energy more than the LUMO energy. The same holds when comparing DSB with HMT (*trans,trans-* 1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene). The comparison between TP and TC shows that 2,5-OR-substitution of the central ring lowers the LUMO and HOMO energies, but that of the LUMO more than of the HOMO. Going from TC to TO introduces para-OR groups on the peripheral rings, which should and does raise the HOMO energy more than the LUMO. It may be noted that these changes in the HOMO/LUMO orbital energies with structure match the red shifts observed in the UV absorption spectra ($\Delta E \approx 0.05 \text{ eV}$ for each p-OCH₃ group and $\Delta E < 0.01 \text{ eV}$ for each m-OCH₃ group in the peripheral rings; $\Delta E \approx 0.10 \text{ eV}$ for 2,5 - OR substitution in the central ring).



Figure 6: Cyclic Voltammogram of TP4 oxidation in dichloromethane using tetrabutylammonium borotetra fluoride as electrolyte at a scan rate of 100 mV sec^{-1} .

Figure 7: Reduction (top) and oxidation potentials (bottom) relative to the standard calomel electrode of compounds. See Fig. 1 for structural formulas.

CONCLUSIONS

In a series of 21 n-alkoxy substituted phenylenevinylene oligomers good solubilities in organic solvents were found for trimers (distyrylbenzenes) substituted in the central ring (TC and TO series). The NMR data of TC and TO compounds show that the preferred conformation of an alkoxy group in ring B is *ortho*- alkoxy- *anti* with respect to the adjacent olefinic link. In fact, the presence of a substituted or the total root of DP and TP compounds do not show a M^{2+} ion, whereas those of TC and TO derivatives do. This observation is consistent with the occurence of higher charged ions in the cyclic voltammograms of the latter compounds and indicates that they more readily lose two electrons upon electron impact than TP⁺ and DP⁺ ions. Mass spectrometry also allows to discriminate between TP, TC and TO compounds from differences in the relative importance of two fragmentation processes: the loss from M⁺ of an alkene molecule (C_nH_{2n}) on the one hand, and the loss of an alkyl radical (R⁺) on the other. As expected, elongation of the conjugated system results in bathochromic (red)

shifts in UV absorption and emission spectra. The following structure-UV activity relations were found: (i) the size of an OR group has no influence, (ii) OR substitution in meta position of a peripheral ring causes a very small red shift, (iii) OR substitution in para position of a peripheral ring causes, by way of a mesomeric interaction, a bathochromic shift of about 12 nm for each OR group, and (iv) OR substitution in the 2,5-positions of the central ring causes, by an inductive interaction over and above the mesomeric effects, an extra large red shift. Excitation spectra showed blue shifts of the $\lambda_{max}(\pi, \pi^*)$ compared to those in absorption.

Reversible cyclic voltammograms of the oligomers are obtained in dichloromethane and Nmethylpyrrolidone solution using tetrabutylammonium borotetrafluoride as supporting electrolyte. In some cases, two or three well separated oxidation and reduction waves could be observed. Taking first oxidation potentials to represent HOMO energies and first reduction potentials to represent LUMO energies, the same relations emerged between structural changes and HOMO/LUMO energies as observed between structural changes and UV red shifts.

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